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Thermochemistry of 1,3-diethylbarbituric and 1, 3-diethyl-2-thiobarbituric acids: Experimental and computational study

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ABSTRACT

This paper reports an experimental and computational thermochemical study on two barbituric acid derivatives, *viz.* 1,3-diethylbarbituric acid and 1,3-diethyl-2-thiobarbituric acid. Values of standard molar enthalpies of formation in the gas phase at $T = 298.15$ K have been derived from experiment. Energies of combustion were measured by the static bomb combustion calorimetry in the case of 1,3-diethylbarbituric acid, and the rotating-bomb combustion calorimetry in the case of 1,3-diethyl-2-thiobarbituric acid. From the combustion energies, standard molar enthalpies of formation in the crystalline state at $T = 298.15$ K were calculated. The enthalpy of vaporization of 1,3-diethylbarbituric acid and enthalpy of sublimation of 1,3-diethyl-2-thiobarbituric acid were determined using the transpiration method. Combining calorimetric and transpiration results, values of $-(611.9 \pm 2.0)$ kJ · mol^{-1} and $-(343.8 \pm 2.2)$ kJ · mol^{-1} for the gas-phase enthalpies of formation at $T = 298.15$ K of 1,3-diethylbarbituric and 1,3-diethyl-2-thiobarbituric acids, respectively, were derived. Theoretical calculations at the G3 and G4 levels were performed, and a study of the molecular structure of the compounds has been carried out. Calculated enthalpies of formation were in very good agreement with the experimental values.

1. Introduction

Over the past years, we have been involved in the study of the thermochemistry of barbituric acid (2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione) and its derivatives, with the aim of understanding the structural effects on their thermodynamic stabilities as reflected in the gas-phase enthalpy of formation. We have published thermochemical studies of the parent compound barbituric acid [1], its 5,5-dimethyl [2], 1,3-dimethyl [3], 5,5-diethyl (barbital) [4,5], 1,3,5-trimethyl, 1,5,5-trimethyl, and 1,3,5,5-tetramethyl [6] derivatives, and also of a sulfur-containing barbituric acid, 2-thiobarbituric acid [7]. We have also reported thermophysical studies of some methyl and ethyl derivatives of barbituric acid [8], and of 2-thiobarbituric acid [9]. Finishing these series of studies, in the present work we have carried out an experimental and computational study on the energy-structure relationships for two ethyl derivatives: 1,3-diethylbarbituric acid (1,3-diethyl-2,4,6(1*H*,3*H*,5*H*)pyrimidinetrione) [CAS 32479-73-5], and 1,3-diethyl-2-thiobarbituric acid (1,3-diethyl-2-thioxodihydro-4,6(1*H*,5*H*)-pyrimidinedione) [CAS 5217-47-0], whose structures are presented in figure 1.

2. Experimental

2.1. Materials and purity control

The preparation and purification of 1,3-diethylbarbituric acid was described in detail in our previous publication [8]. It was re-crystallized from the mixture of chloroform and heptane with a volume ratio of 1.4:1. The 1,3-diethyl-2-thiobarbituric acid was commercially available from Aldrich. This sample was purified by the fractional sublimation. Provenance, purification, and analysis details of the samples under study are given in table 1.

2.2. Static bomb combustion calorimetry

The energy of combustion of 1,3-diethylbarbituric acid was measured in the isoperibol calorimeter equipped with the static bomb. The detailed procedure has been described previously [11]. The solid sample was pressed into a pellet and weighed using

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